PANs Measurements on the C-130 during IMPEX/MIRAGE and INTEX-B

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The INTEX-B study focuses on investigating the chemical and physical composition of air masses over the Gulf of Mexico (IMPEX/MIRAGE) and in air masses advected to the North American continent across the Pacific Ocean (INTEX-B). Specifically, the science objectives of the mission include the following goals:
- quantify the transpacific transport and evolution of Asian pollution to North America and assess its implications for regional air quality and climate;
- quantify the outflow and evolution of gases and aerosols from the Mexico City Megaplex;
- map emissions of trace gases and aerosols and relate atmospheric composition to sources and sinks

More details about the scientific goals of the studies are available on the web for INTEX-B under http://www.espo.nasa.gov/docs/intex-b/INTEX-B_WhitePaper.pdf and for MIRAGE under http://www.ofps.ucar.edu/milagro/.

We plan to contribute to the IMPEX/MIRAGE and INTEX-B campaigns an instrument package for the measurement of peroxyacyl nitrates (PANs, i.e., PAN, PPN, PBN, PBzN, APAN, MPAN, MoPAN, PBzN and others), flown on board the NCAR/NSF C-130 aircraft. In short, PANs are important for a number of the specific science objectives listed above. Enormous amounts of PANs are predicted to be formed and have been measured during previous field campaigns in the Mexico City area. These PANs can contribute significantly to sustain the photochemical reactivity of the plume by releasing NO_x through thermal decomposition as is demonstrated in figure 4 of the MIRAGE scientific overview document. PANs will also be an excellent marker for the plume extent and large-scale impact at least at medium to higher altitudes. Since PANs are a significant part of the NO_y family, the measurement of PANs is essential to understand the NO_y budget and the transformation of the different NO_y species.

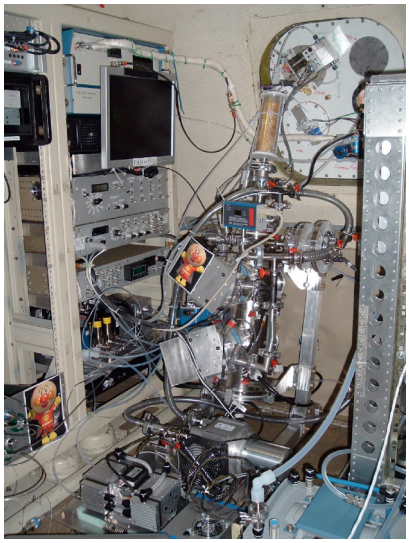
For INTEX-B, PANs are expected to often constitute the dominant fraction of NO_y in Asian plumes observed over the west coast of the United States and are therefore important to quantify both the amount of reactive nitrogen imported and the assessment of the reactivity and ozone formation potential of these air masses.

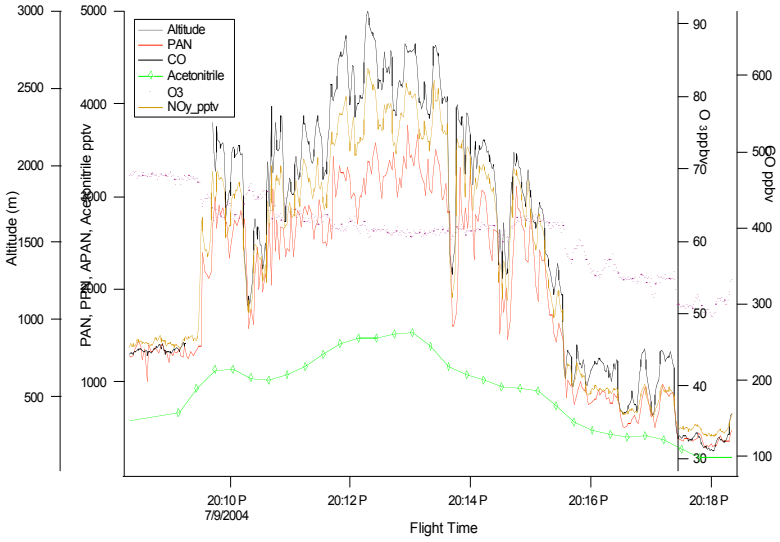
The relative composition of different PANs in the plume can give us information on the hydrocarbon mix contributing to photochemical oxidant formation, the possible influence of biogenic emissions and the emissions from biomass burning.

We will fly our new PAN-CIGARette chemical ionization mass spectrometer which measures up to 7 PAN species simultaneously and semi-continuously with a time resolution of ~2 seconds. The measurement method has been described by Slusher et al. (JGR, 2004). The method is based on the detection of the acylperoxy radicals formed from thermal decomposition of the PAN species at the inlet by reacting them with iodide ions, which are formed by passing methyl iodide diluted in nitrogen through an α–particle source. The reaction of the peroxy acyl radicals with I^- forms IO and the acyl ion, which is detected using a quadrupole mass spectrometer (Extrel) at a mass to charge ratio of 59 in the case of PAN. The method is very specific for PAN type compounds and the limit

of detection is ~1 pptv/s or better for most PAN species. The instrument employs a real-time continuous calibration using isotopically labeled PAN produced in-situ by our photolytic calibration source (Flocke et al, 2005). Data will be available real-time for in-flight planning and preliminary field data will be available within 24 hours of the flight.

A larger prototype version of the instrument (the PAN-CIGAR) has been deployed successfully in the summer of 2004 on board the NOAA P-3 aircraft during the ICARTT campaign. Special consideration will be given to the extreme mixing ratio gradients to be expected between fresh outflow and background air in the Mexico City area and over the Pacific. The figure shows a picture of the prototype instrument installed on the NOAA P3 as well as a demonstration of the time resolution of the data in a plot of data collected during a biomass-burning plume crossing on board the P-3 encountered on June 9, 2004 over Quebec.





Appendix – PAN species:
PAN = peroxyacetyl nitrate
PPN = peroxypropionyl nitrate
PBN = peroxybutyryl nitrate
PBzN = peroxybenzoyl nitrate
MoPAN = methoxyperoxyacetyl nitrate
APAN = peroxyacryloyl nitrate
MPAN = peroxymethacryloyl nitrate
PBzN = peroxybenzoyl nitrate